On the generalized concentration and molecular mass dependencies of macromolecular self-diffusion in polymer solutions

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(Received 23 July 1987; revised 15 January 1988; accepted 15 January 1988)

Self-diffusion experimental data obtained with the n.m.r. pulsed gradient spin–echo method in polyethylene oxide (PEO), polystyrene (PS), dextran, gelatine, cellulose triacetate (CT), poly(dimethyl siloxane) (PDMS) solutions and melts in a wide range of solvents, with molecular mass (M) and concentration (ϕ), were analysed to show the existence of common dependencies for $D_s(M)$ and $D_s(\phi)$. The general law for $D_s(\phi)$ is expressed as $f(\phi/\hat{\phi}) = D_s(\phi)/L(\phi)D_s(0)$ and is correct for the solvent quality ranging from θ to 'good'. The existence of the generalized $f(\phi/\hat{\phi})$ was examined for the 17 different polymer–solvent systems. With the use of the generalized function, where $D_s(0) = \lim_{\phi \to 0} D_s/\hat{\phi}$, $D_s(0) \sim M^{-\beta}$, $\hat{\phi} \sim M^{-\frac{2-\beta}{3}}$, nearly 100 $D_s(\phi)$ dependencies were described. The renormalization function $L(\phi)$ accounts for the local dynamic properties of the concentration dependence.

(Keywords: self-diffusion; generalized function; critical molecular mass; solvent quality)

INTRODUCTION

One of the factors which led to the growth of experimental research in macromolecular self-diffusion in polymer systems was the development of scaling concepts and reptation theory[1,2] of the mechanisms of motion of polymer chains. Such problems as the concentration and molecular mass dependencies of the self-diffusion coefficient, D_s, of the polymer chains remain unsolved in spite of the large quantity of the experimental data collected. For instance, the concentration dependence of D_s is usually discussed only in terms of prediction on the basis of asymptotical scaling laws. In addition, experimental data are usually obtained for a single polymer system over a limited range of concentration and are very often contradictory. Typically, the dependence of D_s on molecular mass (M) shows an absence of any anomalies in the region of the so-called critical entanglement molecular weight (M_c) in most studies[3–5], and the coupling with concentration dependence of D_s is not clarified.

The purpose of the present article is an attempt to find the most common laws for the dependence of $D_s(\phi)$ and $D_s(M)$ on the basis of the analysis of experimental data obtained in different polymer solutions over a wide range of volume concentration (ϕ) and molecular mass, and in a large number of solvents. The main assumption made is that the $D_s(\phi)$ dependence can be described by the universal function $f(\phi/\hat{\phi})$ of the parameter $\phi/\hat{\phi}$, where $\hat{\phi}$ is a critical concentration, depending on polymer molecular mass[6,7]. The pulsed gradient spin-echo method[8–12] was used to measure macromolecular self-diffusion of PS (Pressure Chemical standard) with $M_n = 2 \times 10^3$–7×10^6 ($M_w/M_n \leqslant 1.1$), in benzene (303–353 K), chloroform and cyclohexane (313–333 K), CCl_4 (303–333 K) and dibutylphthalate (313–373 K) solutions; PEO (Fluka-Buchs), with $M_n = 2 \times 10^3$–4×10^4 ($M_w/M_n \lesssim 1.1$) and $M_n = 3 \times 10^6$ ($M_w/M_n \sim 3$) from Union Carbide in dioxane, acetonitrile, benzene (333–363 K) and dibutylphthalate (373 K) solutions; PDMS fractions with $M_n = 1.5 \times 10^4$–7.3×10^5 ($M_w/M_n \leqslant 1.5$) in methylethylketone and toluene (313 K) solutions; dextran (Pharmacia) samples with $M_n = 6 \times 10^3$–2×10^5 ($M_w/M_n \leqslant 2$) in dimethylsulphoxide, formamide and water (303–363 K); a gelatine (Russelot) sample with $M_n = 9 \times 10^4$ ($M_w/M_n \sim 2.2$) in water (313–333 K) and also CT fractions with $M_n = 4.8 \times 10^4$–1.2×10^5 ($M_w/M_n \sim 2.5$) in benzyl alcohol (393–433 K). The maximum concentration varied in the range 3×10^{-3}–1 in PEO and PDMS solutions, 3×10^{-3}–8×10^{-1} in PS solutions, and 3×10^{-3}–4×10^{-1} in solutions of dextran, gelatine and CT.

The range of accessible values of ϕ_s depends on the sensitivity of the n.m.r. apparatus, n.m.r. relaxation properties of macromolecules in solution and also on the low limit (10^{-14}–10^{-15} $m^2 s^{-1}$) of the measurable self-diffusion coefficient.

The polymers studied possess different physicochemical properties, for example, PEO is a crystallizable polymer, PEO and PDMS have their glass transition temperatures much lower, and PS, dextran, gelatine and CT have much higher glass transition temperatures than that measured. The last three polymers are natural products, and dextran is a branched polymer having, on average, one branch every 25–30 units.

The investigations were conducted with the n.m.r. apparatus operating at the ^1H resonance frequency of

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0032–3861/88/071294–07$03.00